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**JAPANESE / ENGLISH TRANSLATION OF**  
**Japanese Patent Application JP 2003 - 155402 A**  
**Polyester Resin Composition for Calendering and Sheet Thereof**

Your Ref: 102203 - 13

For: Eastman Chemical Company

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(19) Japanese Patent Office (JP)

(11) Unexamined Patent Application No:

Kokai 2003-155402

(12) Unexamined Patent Gazette (A)

(P2003-155402A)

(43) Date of Publication: May 30, 2003

(51) Int. Cl. <sup>7</sup>	Class. Symbols	FI	Subject Codes (Reference)
C 08 L 67/02		C 08 L 67/02	4F071
B 29 C 43/24		B 29 C 43/24	4F204
C 08 J 5/18	CFD	C 08 J 5/18	4J002
C 08 K 5/3477		C 08 K 5/3477	
5/372		5/372	

Request for Examination: Not yet submitted

Number of Claims: 8 OL

Total of pages [in original]: 14

(Continued on last page)

(21) Application No.: 2001-356628  
(22) Date of Filing: November 21, 2001

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(Continued on last page)

(54) [Title of the Invention]

Polyester Resin Composition for Calendering  
and Sheet Thereof

(57) [Summary]

[Object] To provide a polyester resin composition that has exceptional properties with regard to the release of molten sheet from the roll during calendering, the takeoff of the sheet from the calendering rolls to the cooling rolls, and good transparency in the resulting sheet.

**[Means of Achievement]** The composition contains an amorphous polyester, a hindered phenolic antioxidant having isocyanurate groups in its molecular skeleton, a thioether antioxidant, and a lubricant. The composition preferably includes 0.05 to 2 parts by weight of the hindered phenolic antioxidant that has isocyanurate groups in its molecular skeleton, 0.01 to 2 parts by weight of the thioether antioxidant, and 0.01 to 5 parts by weight of the lubricant per 100 parts by weight of the amorphous polyester.

**[Claims]**

**[Claim 1]** A polyester resin composition for calendering, characterized by containing an amorphous polyester, a hindered phenolic antioxidant having isocyanurate groups in the molecular skeleton thereof, a thioether antioxidant, and a lubricant.

**[Claim 2]** The polyester resin composition for calendering as described in Claim 1, which contains 0.01 to 2 parts by weight of the hindered phenolic antioxidant having isocyanurate groups in the molecular skeleton thereof, 0.01 to 2 parts by weight of the thioether antioxidant, and 0.01 to 5 parts by weight of the lubricant per 100 parts by weight of the amorphous polyester.

**[Claim 3]** The polyester resin composition for calendering as described in Claim 1 or 2, in which the amorphous polyester is a copolyester that contains terephthalic acid and ethylene glycol as its principal components, and contains either 5 to 50 mol% of isophthalic acid relative to the total carboxylic acid component, or 5 to 50 mol% of one or two or more diols selected from neopentyl glycol, diethylene glycol, 1,4-cyclohexanedimethanol, 2-methyl-1,3-propanediol, and 1,3-propanediol relative to the total diol content.

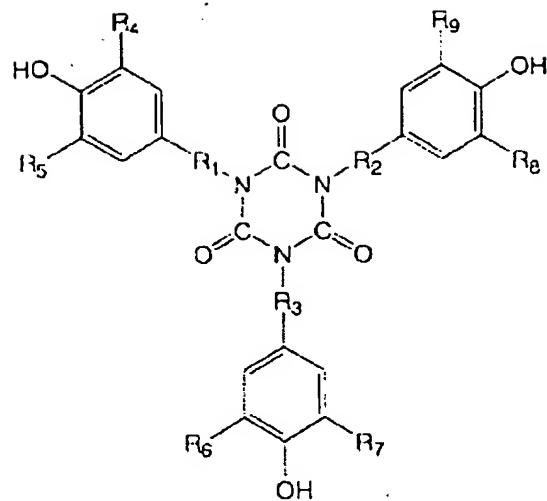
**[Claim 4]** The polyester resin composition for calendering as described in Claim 1 or 2, in which the amorphous polyester is a copolyester that contains terephthalic acid and ethylene glycol as its principal components, and 5 to 50 mol% of one or two or more diols selected from neopentyl glycol, diethylene glycol, and 1,4-cyclohexanedimethanol relative to the total diol content.

**[Claim 5]** The polyester resin composition for calendering as described in Claim 4, in which the copolyester contains at least neopentyl glycol as the diol component.

**[Claim 6]** The polyester resin composition for calendering as described in any of Claims 1 to 5, in which the hindered phenolic antioxidant having an isocyanurate group in the molecular skeleton thereof is a compound as represented by general formula (I) below.

Formula (I):

[Chemical Formula 1]

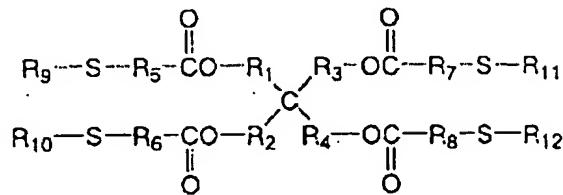


(wherein  $\text{R}_1$  to  $\text{R}_3$  indicate alkylene groups that are either the same or different, and  $\text{R}_4$  to  $\text{R}_9$  indicate methyl groups, ethyl groups, isopropyl groups, or *t*-butyl groups that are either the same or different).

[Claim 7] The polyester resin composition for calendering as described in any one of Claims 1 to 6, in which the thioether antioxidant is a compound as represented by general formula (II) below.

Formula (II):

[Chemical Formula 2]



(wherein  $\text{R}_1$  to  $\text{R}_8$  indicate alkylene groups that are either the same or different, and  $\text{R}_9$  to  $\text{R}_{12}$  indicate alkyl groups that are either the same or different).

[Claim 8] A sheet obtained by means of calendering the polyester resin composition described in any of Claims 1 to 7.

## [Detailed Description of the Invention]

### [0001]

**[Technological Field of the Invention]** The present invention relates to a polyester resin composition and a sheet thereof that has exceptional roll release properties, long-run processing properties, thermal stability, and takeoff from the calendering rolls when calendering polyester resin (hereunder referred to simply as "polyester"); that is suited to calendering for various uses such as sealing labels, aroma-retaining heat seal films, and oil-resistant multilayer sheets for food products, cosmetic products, and beverages; and that is particularly useful as a sheet used in industrial processing.

### [0002]

**[Prior Art]** Conventionally, vinyl chloride sheet (film) has been utilized in a variety of applications because of its low cost and exceptional transparency. The known methods for manufacturing this sheet are extrusion molding and calender molding. In extrusion molding, as compared to calender molding, the workability (moldability) of the resin will vary according to the die lip friction, and the thickness, width, and flow direction of the sheet (film) will be inaccurate; the method is also unsuited for high volume production. For these reasons, calendering has been used more often due to its productivity and quality attributes.

[0003] Sheet may be processed easily (i.e., sheet post-processing is readily accomplished) because the flexibility of the vinyl chloride may be adjusted with comparative ease through the addition of a plasticizer. Typical examples of such applications include decorative sheet (film) imprinted with a wood grain to create the impression of a wood-derived material.

[0004] However, there has been a trend in recent years towards replacing vinyl chloride sheet (hereunder abbreviated as "VC sheet") with other materials in order to control the use of plasticizers, since vinyl chloride may cause harmful gases to be generated when incinerated, and plasticizers are suspected endocrine disrupting substances. Polyester is valued over a number of substitute materials because of its physical properties and cost; however, a major problem is encountered when polyester is used as substitutes, as described hereunder.

[0005] Polyester is not readily suited to calender molding, which is the method that is frequently used in the molding of VC sheet. Conventionally, extrusion molding has primarily been used when manufacturing sheets and films from polyester resin, because processing is

straightforward. However, when polyester resin is subjected to calendering, strong adhesive forces are encountered during thermal plasticization, for which reason the resin readily sticks (adheres) to the rolls when being worked, thereby preventing molding from proceeding smoothly. For this reason, attempts have been made to add various lubricants in order to prevent the resin from sticking (adhering) to the rolls.

[0006] Studies have been made of lubricants such as polyethylene waxes, paraffin wax, and other hydrocarbon lubricants; higher fatty acid lubricants; higher alcohol lubricants; metallic soaps produced from higher fatty acids; fatty acid amide lubricants; and ester lubricants. For example, as disclosed Japanese Patent Application (Kokai) Laid Open Nos. 11-343353, 2000-136294, 2000-186191, 2000-302951, 2001-64496, and 2001-4019 and U.S. Patent No. 6,068,910, cyclohexanedimethanol is copolymerized with polyethylene terephthalate and the degree of crystallinity is reduced to improve workability, and in addition, various lubricants are compounded with the copolyester (amorphous polyester), thereby reducing the adhesiveness of the resin to the roll during thermal plasticization, and resulting in calendered sheet.

[0007] It is disclosed in the aforementioned specifications that the resulting roll release properties are satisfactory; however, the research performed by the present inventors showed major problems in practical application (industrial production). Specifically, when calendering tests were performed using the amorphous polyesters and lubricants described in the aforementioned specifications, the sheet released more readily from the calendering rolls as larger quantities of lubricant were used; however, the strength of the resin melt itself was insufficient when the sheet was released from the calendering rolls, taken off, and then held on the cooling rolls. Accordingly, so-called "sagging" occurred due to the weight of the sheet, which could not be satisfactorily taken from the calendering rolls to the cooling rolls. Specifically, problems were presented in relation to the inadequate takeoff properties of the molten sheet.

[0008]

**[Problems That the Invention Is Intended to Solve]** With the foregoing circumstances in view, it is an object of the present invention to provide a polyester resin composition for calendering and sheet thereof that allows good releasability from the roll to obtained during sheet processing (i.e., when sheets are formed using calendering rolls), that allows good takeoff from the

calendering rolls to be obtained, and that allows sufficiently high transparency to be obtained in the finished sheet.

[0009]

**[Means Used to Solve the Above-Mentioned Problems]** The present inventors conducted intensive research for the purpose of achieving the aforementioned objective. As a result, they perfected the present invention by discovering that the roll release property during calendering, the ability of the molten sheet to be taken off from the calendering rolls, and the transparency of the sheet can be thoroughly improved by means of compounding a lubricant and a specific antioxidant with the amorphous polyester resin.

[0010] Specifically, the present invention has the following characteristics.

(1) A polyester resin composition for calendering, characterized by containing an amorphous polyester, a hindered phenolic antioxidant having isocyanurate groups in its molecular skeleton, a thioether antioxidant, and a lubricant.

(2) The polyester resin composition for calendering as described in (1) above, which contains 0.01 to 2 parts by weight of the hindered phenolic antioxidant having isocyanurate groups in its molecular skeleton, 0.01 to 2 parts by weight of the thioether antioxidant, and 0.01 to 5 parts by weight of the lubricant per 100 parts by weight of the amorphous polyester.

(3) The polyester resin composition for calendering as described in (1) or (2) above, in which the amorphous polyester is a copolyester that contains terephthalic acid and ethylene glycol as its principal components, and contains either 5 to 50 mol% of isophthalic acid relative to the total carboxylic acid component, or 5 to 50 mol% of one or two or more diols selected from neopentyl glycol, diethylene glycol, 1,4-cyclohexanedimethanol, 2-methyl-1,3-propanediol, and 1,3-propanediol relative to the total diol content.

(4) The polyester resin composition for calendering as described in (1) or (2) above, in which the amorphous polyester is a copolyester that contains terephthalic acid and ethylene glycol as its principal components, and 5 to 50 mol% of one or two or more diols selected from neopentyl glycol, diethylene glycol, and 1,4-cyclohexanedimethanol relative to the total diol content.

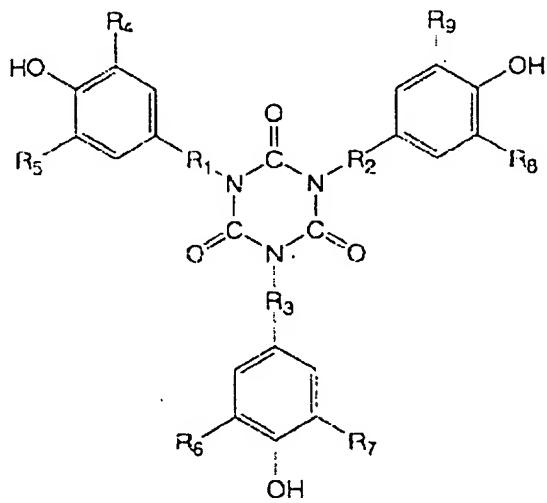
(5) The polyester resin composition for calendering as described in (4) above, in which the copolyester contains at least neopentyl glycol as the diol component.

(6) The polyester resin composition for calendering as described in any one of (1) to (5) above, in which the hindered phenolic antioxidant having an isocyanurate group in its molecular skeleton is a compound as represented by general formula (I) below.

Formula (I):

[0011]

[Chemical Formula 3]



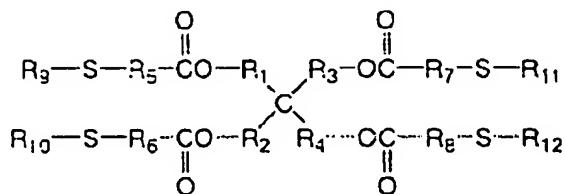
[0012] (wherein R<sub>1</sub> to R<sub>3</sub> indicate alkylene groups that are either the same or different, and R<sub>4</sub> to R<sub>9</sub> indicate methyl groups, ethyl groups, isopropyl groups, or *t*-butyl groups that are either the same or different).

(7) The polyester resin composition for calendering as described in any of (1) to (6) above, in which the thioether antioxidant is a compound as represented by general formula (II) below.

Formula (II):

[0013]

[Chemical Formula 4]



[0014] (wherein R<sub>1</sub> to R<sub>8</sub> indicate alkylene groups that are either the same or different, and R<sub>9</sub> to R<sub>12</sub> indicate alkyl groups that are either the same or different).

(8) A sheet obtained by means of calendering the polyester resin composition described in any of Claims 1 to 7\* above.

[0015]

**[Embodiments of the Invention]** A detailed description of the present invention shall now be provided. The polyester resin composition for calendering of the present invention is characterized by containing an amorphous polyester, a hindered phenolic antioxidant having isocyanurate groups in its molecular structure, a thioether antioxidant, and a lubricant.

[0016] The term "amorphous polyester" that is used in the present invention indicates a polyester that does not have a distinct melt peak in either of two temperature elevation processes performed using a differential scanning calorimeter (DSC); i.e., when the temperature is raised from -100°C to 300°C at a rate of 20°C/min, then cooled from 300°C to -100°C at 50°C/min, and then again raised from -100°C to 300°C at a rate of 20°C/min.

[0017] There are no particular limitations as to the amorphous polyester that is used in the present invention, but from the standpoints of the elongation, strength, and impact resistance of the calendered sheets, polyesters whose principal components are terephthalic acid and ethylene glycol are preferable. The term "principal components" indicates that when the total dicarboxylic acid component and the total diol component are each set to 100 mol%, the two components (terephthalic acid and ethylene glycol) should each be present in an amount of 50 mol% or greater, preferably 60 mol% or greater, and ideally 65 mol% or greater.

[0018] Further, polyesters whose principal components are terephthalic acid and ethylene glycol are preferably of a copolymerization composition that contains (1) 5 to 50 mol% (preferably 10 to 40 mol%) of isophthalic acid relative to the total dicarboxylic acid component, or (2) that contains 5 to 50 mol% (preferably 10 to 40 mol%) of one or two or more diols selected from neopentyl glycol, diethylene glycol, 1,4-cyclohexanedimethanol, 2-methyl-1,3-propanediol, and 1,3-propanediol relative to the total diol component, and are ideally a copolymerization composition that satisfies both (1) and (2) above. In the case of (2) above, the copolymerization

composition preferably contains one or two or more diols selected from among the three diols (neopentyl glycol, diethylene glycol and 1,4-cyclohexanedimethanol). Copolymers that are so configured will have the satisfactory strength, elongation, impact resistance and other properties exhibited by polyethylene terephthalate, and the resin can be made amorphous; therefore, desirable transparency will be obtained. When (2) is satisfied, a polyester having a copolymerization composition that contains neopentyl glycol will have improved compatibility with lubricants (especially the metal salts of organophosphoric acid esters and polyolefin waxes described hereunder), and the quantity of lubricant needed to obtain roll release properties can be decreased. The transparency of the sheets will be thereby advantageously improved, and the strength, elongation, impact resistance, and other mechanical properties of the sheets will be further improved as well.

[0019] Other polyvalent carboxylic acids in addition to isophthalic acid as described above may also be copolymerized in polyesters of this kind whose principal components are terephthalic acid and ethylene glycol. Such polyvalent carboxylic acids include, for example, *o*-phthalic acid, naphthalenedicarboxylic acid, succinic acid, adipic acid, azelaic acid, sebatic acid, decanoic acid, dimer acids, cyclohexanedicarboxylic acid, and trimellitic acid. One or two or more of these acids may be used.

[0020] Other polyhydric alcohol components may also copolymerized in addition to the aforementioned neopentyl glycol, diethylene glycol, 1,4-cyclohexanedimethanol, 2-methyl-1,3-propanediol, and 1,3-propanediol [sic]. Such polyhydric alcohol components can include, for example, 1,3-propylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, hexanediol, nonanediol, dimer diol, ethylene oxide adducts or propylene oxide adducts of bisphenol A, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, 2-butyl-2-ethyl-1,3-propanediol, tricyclodecane dimethanol, hydroxypivalic acid neopentyl ester, 2,2,4-trimethyl-1,5-pentanediol, and trimethylol propane. One or two more of such components may be used.

[0021] Specific examples of amorphous polyesters that are suited for use in the present invention include terephthalic acid / isophthalic acid // ethylene glycol = 90 to 70 / 10 to 30 // 100 mol%; terephthalic acid / isophthalic acid // ethylene glycol / 1,3-propylene glycol = 95 to 80 / 5 to 20 // 90 to 70 / 10 to 30 mol%; terephthalic acid / isophthalic acid // ethylene glycol / 1,4-butanediol =

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[Translator's note: this is most likely a typographical error. It is presumed that what is meant is "...any of (1) to (7) above...". in

95 to 70 / 5 to 30 // 90 to 50 / 10 to 50 mol%; terephthalic acid // ethylene glycol / 2-methyl-1,3-propanediol = 100 / 60 to 80 / 40 to 20 mol%; terephthalic acid / isophthalic acid // ethylene glycol / 2-methyl-1,3-propanediol = 95 to 80 / 5 to 20 // 70 to 90 / 30 to 10 mol%; terephthalic acid // ethylene glycol / neopentyl glycol = 100 / 85 to 60 / 15 to 40 mol%; terephthalic acid / isophthalic acid // ethylene glycol / neopentyl glycol = 95 to 80 / 5 to 20 // 90 to 70 / 10 to 30 mol%; terephthalic acid // ethylene glycol / diethylene glycol = 100 // 75 to 50 / 25 to 50 mol%; terephthalic acid / isophthalic acid // ethylene glycol / diethylene glycol = 95 to 80 / 5 to 20 // 90 to 75 / 10 to 25 mol%; and terephthalic acid // ethylene glycol / 1,4-cyclohexane dimethanol = 100 // 80 to 60 / 20 to 40 mol%. With these amorphous polyesters, it will be possible to obtain a suitable amorphous state, the transparency of the worked sheets will be increased further, and the glass transition temperatures will be suitably adjustable over the ranges below. Among the aforementioned amorphous polyesters, terephthalic acid // ethylene glycol / neopentyl glycol = 100 // 85 to 60 / 15 to 40 mol%; terephthalic acid / isophthalic acid // ethylene glycol / neopentyl glycol = 95 to 80 / 5 to 20 / 90 to 70 / 10 to 30 mol%; terephthalic acid // ethylene glycol / diethylene glycol = 100 // 75 to 50 / 25 to 50 mol%; terephthalic acid / isophthalic acid // ethylene glycol / diethylene glycol = 95 to 80 / 5 to 20 // 90 to 75 / 10 to 25 mol%; and terephthalic acid // ethylene glycol / 1,4-cyclohexanedimethanol = 100 // 80 to 60 / 20 to 40 mol% are ideal because the balance between the roll release properties, the ability for the molten sheet to be taken off from the calendering rolls, and the transparency of the finished sheet can be kept at a high level.

[0022] The lower limit of the number average molecular weight of the amorphous polyesters used in the present invention is preferably 15000, more preferably 18000, and ideally 20000. The upper limit is preferably 40000, and ideally 35000. If the number average molecular weight is less than 15000, the aggregating power of the resin will be inadequate, for which reason the strength and elongation of the resulting sheet are insufficient, thereby rendering it brittle and unusable. On the other hand, if it is greater than 40000, the melt viscosity will increase, for which reason the optimum temperature for calendering is also increased, thereby worsening the roll release properties.

[0023] The acid value of the amorphous polyester that is used in the present invention is preferably 60 eq/10<sup>6</sup> g or less, more preferably 50 eq/10<sup>6</sup> g or less, and ideally 40 eq/10<sup>6</sup> g or

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keeping with the logic of the other paragraphs above.]

less. If the acid value exceeds 60 eq/10<sup>6</sup> g, hydrolysis will proceed further, and the mechanical strength of the resulting sheet will decrease when the resin is heated during calendering. The ability of the sheet to be released from the roll will also decrease as the resin continues to decompose.

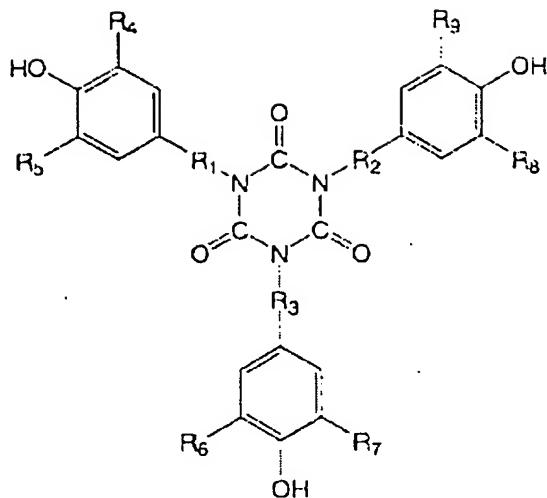
[0024] In the present invention, the amorphous polyester is compounded with at least a lubricant, a hindered phenolic antioxidant having isocyanurate groups in its molecular skeleton, and a thioether antioxidant. Specifically, there are various compounds known as antioxidants for use with plastics, and when the amorphous polyester is subjected to calendering, molten sheet that has been formed by means of the calendering rolls will be better able to be transferred to the cooling rolls from the calendering rolls (i.e., sagging can be prevented), if a thioether antioxidant has been combined with a hindered phenolic antioxidant having an isocyanurate group in its molecular skeleton, and if these components are compounded with a lubricant in the amorphous polyester. This will also allow sufficiently high- transparency sheet to be manufactured as the end product. A similar effect is not obtained when a hindered phenolic antioxidant that does not have isocyanurate groups in its molecular skeleton is used in combination with a thioether antioxidant.

[0025] In the present invention, there are no particular limitations as to the hindered phenolic antioxidant that has isocyanurate groups in its molecular skeleton. However, compounds as represented by general formula (I) below are preferred.

Formula (I):

[0026]

[Chemical Formula 5]



[0027] (wherein R<sub>1</sub> to R<sub>3</sub> indicate alkylene groups that are either the same or different, and R<sub>4</sub> to R<sub>9</sub> indicate methyl groups, ethyl groups, isopropyl groups, or *t*-butyl groups that are either the same or different).

[0028] In the compounds of formula (I), the alkylene group represented by R<sub>1</sub> to R<sub>3</sub> in the formula preferably has 1 to 3 carbons; e.g., a methylene group, an ethylene group or a propylene group. In addition, R<sub>1</sub> to R<sub>3</sub> are preferably the same.

[0029] In the formula, the alkylene groups represented by R<sub>4</sub> to R<sub>9</sub> are preferably the same, in which case methyl groups, isopropyl groups and *t*-butyl groups are desirable, with *t*-butyl groups being particularly desirable.

[0030] A specific example of a particularly desirable compound of formula (I) is *tris*(3,5-di-*t*-butyl-4-hydroxybenzyl)isocyanurate in which R<sub>1</sub> to R<sub>3</sub> are methylene groups and R<sub>4</sub> to R<sub>9</sub> are *t*-butyl groups. *Tris*(3,5-di-*t*-butyl-4-hydroxybenzyl)isocyanurate is particularly desirable not only from the standpoint of the takeoff properties (ability of the sheet to be transferred from the calendering rolls to the cooling rolls) of the target molten sheet, but from the standpoints of universal utility and economic considerations as well.

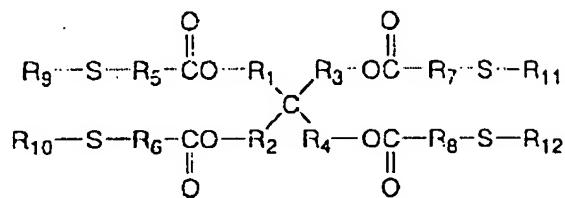
[0031] In the present invention, the lower limit of the compounded amount of hindered phenol antioxidant having isocyanurate groups in its molecular skeleton (per 100 parts by weight of

amorphous polyester) is 0.01 parts by weight, preferably 0.02 parts by weight, and ideally 0.05 parts by weight. The upper limit is preferably 2 parts by weight, more preferably 1.8 parts by weight, and ideally 1.5 parts by weight. If the compounded amount is less than 0.01 parts by weight, the molten sheet may not be able to be taken off satisfactorily. On the other hand, if the compounded amount exceeds two parts by weight, decreased compatibility with the amorphous polyester will result, the sheet will lose its transparency, and when the sheets are used over long periods of time, the antioxidant may bleed out, thereby worsening the external sheet appearance. [0032] In the present invention, the term "thioether antioxidant" refers to an antioxidant having thioether groups in its molecules. There are no particular limitations as to such antioxidants, with examples including dilauryl-3-3'-thiodipropionate, dimyristyl-3,3'-thiodipropionate, distearyl-3,3'-thiodipropionate (among which distearyl-3,3'-thiodipropionate is preferred), and compounds as indicated by general formula (II) indicated below. Ideal among these compounds are those indicated by general formula (II) below. Such thioether antioxidants may be used individually or in combinations of two or more.

Formula (II):

[0033]

[Chemical Formula 6]



[0034] (wherein R<sub>1</sub> to R<sub>8</sub> indicate alkylene groups that are either the same or different, and R<sub>9</sub> to R<sub>12</sub> indicate alkyl groups that are either the same or different).

[0035] In compounds of formula (II), it is desirable that there be one to three carbons in R<sub>1</sub> to R<sub>4</sub>, as with methylene groups, ethylene groups, and propylene groups. R<sub>1</sub> to R<sub>4</sub> are preferably the same. R<sub>5</sub> to R<sub>8</sub> preferably have one to four carbons, as with methylene groups, ethylene groups, propylene groups, or butylene groups. R<sub>5</sub> to R<sub>8</sub> are preferably the same. R<sub>9</sub> to R<sub>12</sub> preferably have 6 to 18 carbons, and are preferably the same. A particularly preferred example of a

compound of formula (II) is pentaerythritol *tetrakis*(3-laurylthiopropionate) in which R<sub>1</sub> to R<sub>4</sub> are methylene groups, R<sub>5</sub> to R<sub>8</sub> are ethylene groups, and R<sub>9</sub> to R<sub>12</sub> are lauryl groups.

[0036] Pentaerythritol *tetrakis*(3-laurylthiopropionate) is particularly desirable not only from the standpoint of the takeoff properties of the target molten sheet (i.e., the ability of the sheet to be transferred from the calendering rolls to the cooling rolls), but from the standpoints of universal utility and economic considerations as well.

[0037] In the present invention, the thioether antioxidant is compounded with the aforementioned hindered phenolic antioxidant that has isocyanurate groups in its molecular skeleton, thereby dramatically improving the ability of the molten sheet to be taken off from the rolls. In other words, the use of a comparatively small quantity of thioether antioxidant together with the hindered phenolic antioxidant that has isocyanurate groups in its molecular skeleton dramatically improves the takeoff properties of the molten sheet, as compared to when only the hindered phenolic antioxidant that has isocyanurate groups in its molecular skeleton is used. As a result, good molten sheet takeoff properties are obtained without a decrease in the transparency of the polyester. The lower limit of the compounded amount of thioether antioxidant (per 100 parts by weight of amorphous polyester) is preferably 0.01 parts by weight, more preferably 0.02 parts by weight, and ideally 0.05 parts by weight. The upper limit is preferably 2 parts by weight, more preferably 1.8 parts by weight, and ideally 1.5 parts by weight. If the amount is less than 0.01 parts by weight, adequate roll takeoff properties may not always be obtained. If the amount is more than 2 parts by weight, compatibility with the amorphous polyester will decrease, the sheet will lose its transparency, and when the sheet is used over long periods of time, the antioxidant may bleed out, thereby worsening the external sheet appearance.

[0038] Antioxidants other than the aforementioned thioether antioxidants and hindered phenolic antioxidants that have isocyanurate groups in their molecular skeletons may be added to the polyester resin in order to prevent heat degradation of the polyester resin of the present invention during processing (i.e., to prevent the resin from being colored as a result of heat degradation). Examples of preferred alternative antioxidants include phenolic antioxidants and organic phosphorous acid ester compounds.

[0039] Specific examples of phenolic antioxidants include 2,6-di-*tert*-butylphenol, 2,6-di-*tert*-butyl-4-methylphenol, 2,6-di-*tert*-butyl-4-ethylphenol, 2-*tert*-butyl-4,6-dimethylphenol, 2,4,6-tri-*tert*-butylphenol, 2-*tert*-butyl-4-methoxyphenol, 3-methyl-4-isopropylphenol, 2,6-di-*tert*-butyl-4-

hydroxymethylphenol, 2,2-bis(4-hydroxyphenyl)propane, *bis*(5-*tert*-butyl-4-hydroxy-2-methylphenyl)sulfide, 2,5-di-*tert*-amyl hydroquinone, 2,5-di-*tert*-butylhydroquinone, 1,1-*bis*(3-*tert*-butyl-4-hydroxy-5-methylphenyl)butane, *bis*(3-*tert*-butyl-2-hydroxy-5-methylphenyl)methane, 2,6-*bis*(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)-4-methylphenol, *bis*(3-*tert*-butyl-4-hydroxy-5-methylbenzyl)sulfide, *bis*(3-*tert*-butyl-5-ethyl-2-hydroxyphenyl)methane, *bis*(3,5-di-*tert*-butyl-4-hydroxyphenyl)methane, *bis*(3-*tert*-butyl-2-hydroxy-5-methylphenyl)sulfide, 1,1-*bis*(4-hydroxyphenyl)cyclohexane, ethylene *bis*[3,3-*bis*(3-*tert*-butyl-4-hydroxyphenyl)butyrate], *bis*[2-(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)-4-methyl-6-*tert*-butylphenyl]terephthalate, 1,1-*bis*(2-hydroxy-3,5-dimethylphenyl)-2-methylpropane, 4-methoxyphenol, cyclohexyl phenol, *p*-phenylphenol, catechol, hydroquinone, 4-*tert*-butyl pyrocatechol, ethyl gallate, propyl gallate, octyl gallate, lauryl gallate, cetyl gallate,  $\beta$ -naphthol, 2,4,5-trihydroxybutyropheneone, 1,3,5-trimethyl-2,4,6-*tris*(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene, 1,6-*bis*[2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyloxy] hexane, *tetrakis*[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyloxy-methyl]methane, *tetrakis*[methylene-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate]methane, *bis*(3-cyclohexyl-2-hydroxy-5-methylphenyl)methane, *bis*[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyloxyethyl]sulfide, *n*-octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate, *bis*[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionylamino] hexane, 2,6-*bis*(3-*tert*-butyl-2-hydroxy-5-methylphenyl)-4-methylphenol, *bis*[S-(4-*tert*-butyl-3-hydroxy-2,6-dimethylbenzyl)]thiobenzoate, and 1,1,3-*tris*(3-*tert*-butyl-4-hydroxy-6-methylphenyl)butane. These compounds may be used individually or in combinations of two or more.

[0040] The upper limit of the compounded amount of this phenolic antioxidant (per 100 parts by weight of amorphous polyester) is preferably 1.0 parts by weight or less, and especially preferably 0.8 parts by weight or less. The lower limit is preferably 0.01 parts by weight or greater, and especially preferably 0.02 parts by weight or greater. If the compounded amount is less than 0.01 parts by weight, the effect of inhibiting heat degradation during processing will become difficult to obtain. If the amount exceeds 1.0 parts by weight, the effect of inhibiting thermal deterioration will become saturated, which is not economically advantageous.

[0041] Specific examples of organic phosphorous acid ester compounds include triphenyl phosphite, *tris*(methylphenyl) phosphite, triisooctyl phosphite, tridecyl phosphite, *tris*(2-ethylhexyl) phosphite, *tris*(nonylphenyl) phosphite, *tris*(octylphenyl) phosphite, *tris*[decylpoly(oxyethylene)] phosphite, *tris*(cyclohexylphenyl) phosphite, tricyclohexyl phosphite, tri(decyl)

thiophosphite, triisodecylthiophosphite, phenyl · *bis*(2-ethylhexyl) phosphite, phenyl · diisodecyl phosphite, tetradecylpoly(oxyethylene) · *bis* (ethylphenyl) phosphite, phenyl · dicyclohexyl phosphite, phenyl · diisoctyl phosphite, phenyl · *di*(tridecyl) phosphite, diphenyl · cyclohexyl phosphite, diphenyl · isoctyl phosphite, diphenyl · 2-ethylhexyl phosphite, diphenyl · isodecyl phosphite, diphenyl · cyclohexylphenyl phosphite, diphenyl · (tridecyl) thiophosphite, nonylphenyl · ditridecyl phosphite, phenyl · *p-tert*-butylphenyl · dodecyl phosphite, diisopropyl phosphite, *bis*[octadecylpoly(oxyethylene)] phosphite, octylpoly(oxypropylene) · tridecylpoly(oxypropylene) phosphite, monoisopropyl phosphite, diisodecyl phosphite, diisoctyl phosphite, monoisoctyl phosphite, didodecyl phosphite, monododecyl phosphite, dicyclohexyl phosphite, monocyclohexyl phosphite, monododecyl(oxyethylene) phosphite, *bis*(cyclohexylphenyl) phosphite, monocyclohexyl · phenyl phosphite, *bis*(*p-tert*-butylphenyl) phosphite, tetratridecyl · 4,4'-isopropylidene diphenyl diphosphite, tetratridecyl · 4,4'-butylidene *bis*(2-*tert*-butyl-5-methylphenyl) diphosphite, tetraisoctyl · 4,4'-thiobis(2-*tert*-butyl-5-methylphenyl) diphosphite, *tetrakis*(nonylphenyl) · poly(propyleneoxy)isopropyl diphosphite, *tetratri-decyl* · propylene oxypropyl phosphite, tetratridecyl · 4,4'-isopropylidene dicyclohexyl diphosphite, *pentakis*(nonylphenyl) · *bis*[poly(propyleneoxy)isopropyl] triphosphite, *heptakis*(nonylphenyl) · *tetrakis*[poly(propyleneoxy)isopropyl] pentaphosphite, *heptakis* (nonylphenyl) · *tetrakis*(4,4'-isopropylidenediphenyl) pentaphosphite, *dekkakis*(nonyl-phenyl) · *heptakis*(propyleneoxyisopropyl) octaphosphite, decaphenyl · *heptakis*(propyleneoxyisopropyl) octaphosphite, *bis*(butoxy-carboethyl) · 2,2-dimethylene-trimethylene dithiophosphite, *bis*(isoctoxycarbomethyl) · 2,2-dimethylene trimethylene dithiophosphite, tetradodecyl · ethylene dithiophosphite, tetradocecyldihexamethylene dithiophosphite, tetradoecyl · 2,2'-oxydiethylene dithiophosphite, pentadodecyl · di(hexamethylene) trithiophosphite, diphenyl phosphite, 4,4'-isopropylidene-dicyclohexyl phosphite, 4,4'-isopropylidene diphenyl · alkyl (C12 to C15) phosphite, 2-*tert*-butyl-4-[1-(3-*tert*-butyl-4-hydroxyphenyl)isopropyl] phenyldi(*p*-nonylphenyl) phosphite, ditridecyl · 4,4'-butylidene*bis*(3-methyl-6-*tert*-butylphenyl) phosphite, dioctadecyl · 2,2-dimethylene trimethylene diphosphite, *tris* (cyclohexylphenyl) phosphite, hexatridecyl · 4,4',4"-1,1,3-butanetolyl-*tris*(2-*tert*-butyl-5-methylphenyl) triphosphite, tridodecyl thiophosphite, decaphenyl · *heptakis*(propylene-oxyisopropyl) octaphosphite, dibutyl · *pentakis*(2,2-dimethylene-

trimethylene) diphosphite, dioctyl *pentakis*(2,2-dimethylenetrimethylene) diphosphite, didecy 2,2-dimethylenetrimethylene diphosphite, and lithium, sodium, potassium, magnesium, calcium, barium, zinc and aluminum metal salts thereof. These compounds may be used individually or in combinations of two or more.

[0042] The upper limit of the compounded amount of the organic phosphorous acid ester compound (compounded amount per 100 parts by weight of the amorphous polyester) is preferably 3.0 parts by weight or less, and more preferably 2.0 parts by weight or less. The lower limit is preferably 0.01 parts by weight or greater, and more preferably 0.02 parts by weight or greater. If the compounded amount is less than 0.01 parts by weight, the effect of inhibiting heat degradation during processing will become difficult to obtain. If the amount exceeds 3.0 parts by weight, the effect of inhibiting thermal deterioration will become saturated, which is not economically advantageous.

[0043] In the present invention, a lubricant is compounded with the amorphous polyester in order to reduce adhesion between the amorphous polyester and the calendering rolls (i.e., to improve the release properties of the molten sheet with regard to the rolls).

[0044] The amount of lubricant compounded (per 100 parts by weight of amorphous polyester) is preferably 0.01 to 5 parts by weight. The lower limit is preferably 0.05 parts by weight, more preferably 0.1 parts by weight, and ideally 0.2 parts by weight. The upper limit is preferably 4.5 parts by weight, more preferably 4 parts by weight, and ideally 3.5 parts by weight. If the amount of lubricant is less than 0.01 parts by weight, the roll release property-improving effect will become difficult to obtain. If the amount exceeds 5 parts by weight, there will be a tendency for the transparency, non-colorability, and printability of the worked sheet to deteriorate.

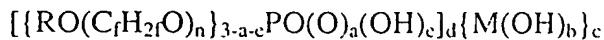
[0045] Examples of lubricants for use in the present invention include polyolefin waxes; metal salts of organophosphoric acid esters; organophosphoric acid esters; ester compounds of adipic acid or azelaic acid and higher aliphatic alcohols; fatty acid amides such as ethylenebis(stearamide), methylenebis(stearamide) and ethylenebis(oleamide); glycerin high fatty acid ester compounds; pentaerythritol higher fatty acid ester compounds; higher fatty acid alcohols; higher fatty acids; paraffins derived from petroleum or coal; waxes; natural or synthetic polymer ester waxes; and metallic soaps made from higher fatty acids. These lubricants may be used individually or in combinations of two or more. From the standpoints of having the sheet be releasable from the roll and the finished sheet be transparent, polyolefin wax and/or metal

salts of organophosphoric acid esters are preferably used. The combined use of polyolefin waxes and metal salts of organophosphoric acid esters is particularly desirable.

[0046] Examples of the polyolefin waxes that are used as lubricants in the present invention include polyethylene waxes, polypropylene waxes, and derivatives thereof. These derivatives include copolymers with other monomers, such as acrylic acid, vinyl acetate, styrene, and maleic acid, and partially oxidized decomposition products thereof.

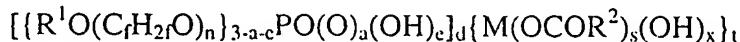
[0047] Examples of metal salts of organophosphoric acid esters to be used as lubricants in the present invention include metal salts of organophosphoric acid esters as indicated by general formula (III) below and/or metal salts of organophosphoric acid esters as indicated by general formula (IV) below.

[0048] Formula (III):



[0049] (wherein R is a hydrocarbon group of 4 to 30 carbons, M is an alkali metal, alkaline-earth metal, Zn, or Al, a is 1 or 2, e is 0 or 1 (but 0 or 1 when a is 1, and 0 when a is 2), b is 0 to 2, c is 1 or 2, d is 1 to 3, f is 2 or 3, n is 0 to 60, and a, b, c, and d have the following relationship with the valence (hereunder indicated as m) of the metal (M): when m = 1, b = 0, d = 1, and a = c; when m is 2, b = 0, c = 1, a × d = 2, or b = 1, d = 1, and a = c; when m = 3, b = 0, d = 3, a = c, b = 1, c = 1, and a × d = 2, or b = 2, d = 1, and a = c. When m ≥ 2, mutually different phosphate ion groups may also be bonded to the metal (M). In this case, d = 2 or 3 is the total number of phosphate ion groups that are mutually different. Further, when d is 2 or 3, the respective structures in brackets may be the same or different from each other.).

[0050] Formula (IV):



[0051] (wherein R<sup>1</sup> is a hydrocarbon group of 4 to 30 carbons, R<sup>2</sup> is an alkyl group of 1 to 25 carbons, M is an alkali metal, alkaline-earth metal, Zn, or Al, a is 1 or 2, e is 0 or 1 (but is 0 or 1 when a is 1, and is 0 when a is 2), d = 1 or 2, s is 1 or 2, x is 0 or 1, t is 1 or 2, f is 2 or 3, and n is 0 to 60. s + x = 1 or 2, and a, d, s, and t have the following relationship with the valence (hereunder indicated as m) of the metal (M): when m = 2, s = 1, d = 1, and a = t; when m = 3, s = 1, t = 1, and a × d = 2, or s = 2, d = 1, and a = t. Further, when m = 3, mutually different phosphate ion groups may be bonded with the metal (M). In this case, d = 2 signifies the total

number of phosphate ion groups. Further, when d is 2, the respective structures in brackets may be the same or different from each other.)

[0052] Alkyl groups, phenyl groups, arylalkyl groups, alkenyl groups, or alkyl phenyl groups are preferred as the hydrocarbon groups of 4 to 30 carbons indicated by R in general formula (III) and the hydrocarbon groups of 4 to 30 carbons indicated by R<sup>1</sup> in general formula (IV).

Examples of the alkali metals that are represented by M in general formula (III) and general formula (IV) include Li, Na, and K, and examples of the alkaline-earth metals include Mg, Ca, and Ba.

[0053] The metal salts of the organophosphoric acid esters represented by general formula (III) and the metal salts of the organophosphoric acid esters represented by general formula (IV) may be manufactured by means of common methods, and there are no particular limitations as regards to such methods of manufacture.

[0054] Preferred examples of the metal salts of the organophosphoric acid esters represented by general formula (III) include compound (1) to compound (13) in Table 1 below and compound (14) to compound (16) in Table 2 below. Preferred examples of the metal salts of the organophosphoric acid esters represented by general formula (IV) include compound (17) to compound (26) in Table 2 below.

[0055] These compounds (compound (1) to compound (26)) are mixtures (compositions) of a plurality of phosphoric acid metal salts in which the number of repeating oxyethylene units or oxytrimethylene units in the polyether alcohol component may be the same or different, such that the number of repetitions of the oxyethylene units or oxytrimethylene units in the polyether alcohol component (i.e., the number of repetitions (n) in the formula  $(C_fH_2O)_n$ ) is a number that includes a decimal fraction.

[0056]

[Table 1]

Cmpd No.	Structural formula	Cmpd No.	Structural formula
(1)	$\text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{3,4} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{Na}$	(9)	$\left[ \text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \right] \text{ZnOH}$
(2)	$\text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{3,4} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{Li}$	(10)	$\left[ \text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \right] \text{Al(OH)}$
(3)	$\text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{Ca}$		$\text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{OH}$
(4)	$\text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{OMgOH}$		$\left[ \text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \right] \text{Mg}$
(5)	$\text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{Al(OH)}$	(11)	$\text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{OK}$
(6)	$\left[ \text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \right] \text{P} \text{OK}$		
(7)	$\left[ \left( \text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \right] \text{P} \text{O} \text{Zn}$	(12)	$\text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{Li}$
(8)	$\text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{Zn}$	(13)	$\text{C}_6\text{H}_5 \left( \text{OCH}_2\text{CH}_2 \right)_{6,6} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{OZnOEt}$

[0057]

[Table 2]

Cmpd No.	Structural formula	Cmpd No.	Structural formula
(14)	$\text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \right)_{3,4} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{Na}$	(21)	$\text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{C}_6\text{H}_5\text{COO} \text{Al}$
(15)	$\left[ \text{C}_6\text{H}_5 \text{CH}_2 \text{CH}_2 \left( \text{OCH}_2\text{CH}_2 \right)_{3,4} \text{O} \right]_2 \text{P} \text{O} \text{Ca}$	(22)	$\left[ \text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \right]_2 \text{P} \text{O} \text{C}_6\text{H}_5\text{COO} \text{Al(OH)}$
(16)	$\text{C}_{21}\text{H}_{44} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{Zn}$	(23)	$\left[ \text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \right]_2 \text{P} \text{O} \text{C}_6\text{H}_5\text{COO} \text{ZnO}$
(17)	$\text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{C}_6\text{H}_5\text{COO} \text{BaO}$	(24)	$\text{C}_6\text{H}_5 \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{C}_6\text{H}_5\text{COO} \text{CaO}$
(18)	$\text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{C}_6\text{H}_5\text{COO} \text{MgO}$	(25)	$\text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2\text{CH}_2 \right)_{11,2} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{C}_6\text{H}_5\text{COO} \text{BaO}$
(19)	$\text{C}_{16}\text{H}_{33} \left( \text{CCH}_2\text{CH}_2 \right)_{11,5} \text{O} \begin{array}{c} \text{O} \\ \parallel \\ \text{P} \end{array} \text{O} \text{C}_6\text{H}_5\text{COO} \text{CaO}$	(26)	$\left( \text{C}_{16}\text{H}_{33} \text{O} \right)_{12} \text{P} \text{O} \text{C}_6\text{H}_5\text{COO} \text{ZnO}$
(20)	$\left[ \text{C}_{16}\text{H}_{33} \left( \text{OCH}_2\text{CH}_2 \right)_{4,5} \text{O} \right]_2 \text{P} \text{O} \text{C}_6\text{H}_5\text{COO} \text{ZnO}$		

[0058] Other additives may also be added in appropriate quantities to the polyester composition of the present invention depending on the use of the calendered sheet. Examples of such additives include fillers, ultraviolet absorbers, photostabilizers, pigments, antistatic agents, antibacterial agents, epoxy compounds, crosslinking agents and sulfur-based antioxidants.

[0059] The aforementioned components of the polyester resin composition for calendering of the present invention are mixed using a known mixing device such as a Henschel mixer, and the mixture is kneaded with mixing rolls, warming rolls, a Banbury mixer, or the like, and then supplied for calendering.

[0060] The melt viscosity of the polyester resin composition of the present invention when the shear rate is  $100\text{ sec}^{-1}$  at  $22^\circ\text{C}$  is preferably 6000 dPa·sec or greater, more preferably 7000 dPa·sec or greater, and ideally 8000 dPa·sec or greater. The upper limit is preferably 60000 dPa·sec or less, more preferably 50000 dPa·sec or less, and ideally 40000 dPa·sec or less. If the melt viscosity is less than 6000 dPa·sec, the adhesiveness of the resin will increase, and the ability of a sheet made from this type of polyester resin composition to be releasable from the roll may decrease as a result. On the other hand, if the melt viscosity exceeds 60000 dPa·sec, the melt viscosity of the polyester resin composition will be excessively high, and productivity will decline.

[0061] There are no particular limitations as to the temperature of the rolls when the polyester resin composition of the present invention is to be calendered, but a preferred temperature is approximately 160 to  $200^\circ\text{C}$ , with 170 to  $190^\circ\text{C}$  being particularly desirable.

[0062] The polyester resin composition of the present invention has exceptional roll release properties, whereby the time for the composition to adhere to the heated roll at  $180^\circ\text{C}$  during calendering (i.e., the time from the start of kneading to when the composition completely adheres to the heated roll) is 15 minutes or more.

[0063] Further, the polyester resin composition of the present invention is suitable for calendering (i.e., the worked sheet is highly transparent), because a haze of 15% or less will result when the composition is calendered and thereby formed into a sheet that is 0.7 mm thick, which has been unachievable with conventional polyester resin compositions.

[0064] The thickness of the sheet that is obtained when the polyester resin composition of the present invention is subjected to calendering will vary according to the sheet application, but is

normally 10 to 1000  $\mu\text{m}$ , and preferably 30 to 800  $\mu\text{m}$ . The term "sheet" shall also imply thin articles that are frequently referred to as "film."

[0065] The sheet of the present invention is ideal for applications such as sealing labels for food products, cosmetic products, and beverages; aroma-retaining heat seal films; oil-resistant multilayer sheets; and sheets for construction use, foodstuff packing containers, blister packs, and stationery. The sheet is particularly suited for use in construction, food product packaging containers, blister packs, and stationery, where particularly high transparency is demanded. The sheet is not only highly transparent, but uses amorphous polyesters, which are advantageous in being able to readily undergo thermal plasticization and being comparatively easy to work.

Therefore, the sheet may be used as decorative sheet that is to be printed.

[0066] The methods used to measure specific values in the present specification shall be described below.

(1) Composition of polyester resin

The resin was dissolved in heavy chloroform and quantified using  $^1\text{H-NMR}$ .

(2) Glass transition temperature of the polyester resin

A differential scanning calorimeter was used, and 10 mg of a measurement sample was introduced into an aluminum pan, which was then covered and sealed. Measurements were made at a temperature elevation rate of 20°C/min.

(3) Number average molecular weight of the polyester resin

The number average molecular weight was determined as a value for polystyrene by means of gel permeation chromatography, using hexafluoroisopropanol as a solvent.

(4) Acid value of the polyester resin

The acid value was determined by dissolving the resin in chloroform and performing titration with a 0.1 N potassium hydroxide ethanol solution. Phenol phthalein was used as the indicator.

[0067]

[Working Examples] The present invention shall be described in greater detail below by way of working examples; however, the present invention shall not be limited in any way to the examples described below.

[0068] (Example of synthesis of amorphous polyester)

(Amorphous polyester A) 960 parts by weight of dimethyl terephthalate, 580 parts by weight of ethylene glycol, 170 parts by weight of neopentyl glycol, and 0.34 parts by weight of tetrabutyl titanate were introduced into a reaction chamber equipped with a stirrer, temperature gauge, and a cooling device for effluent, and transesterification was performed for two hours at 170 to 220°C. After the ester interchange reaction was complete, the temperature of the reaction system was raised from 220°C to 270°C, while the pressure inside the system was slowly decreased over a period of 60 minutes to 500 Pa. A polycondensation reaction was then performed for 55 minutes at 130 Pa or less, resulting in amorphous polyester A. Analyzing amorphous polyester A using NMR revealed that its composition consisted of 100 mol% terephthalic acid as the dicarboxylic acid component, 75 mol% ethylene glycol as the diol component, and 25 mol% neopentyl glycol. The glass transition temperature was 78°C, the number average molecular weight was 26000, and the acid value was 27 eq/10<sup>6</sup> g.

[0069] (Amorphous polyesters B to E) Amorphous polyesters B to E having the compositions (the numerals being mol% in the resin) and physical properties shown in Table 3 were synthesized by the same method used for amorphous polyester A.

[0070]

[Table 3]

		Amorphous polyesters				
		A	B	C	D	E
Acid	Terephthalic acid	100	90	88	85	100
	Isophthalic acid		10		15	
	Adipic acid			12		
Diol	Ethylene glycol	75	83	75	70	69
	Diethylene glycol		17			
	Neopentyl glycol	25				
	1,4-cyclohexanedimethanol					31
	2-methyl-1,3-propanediol			25		
	1,3-propanediol				30	
Physical properties	Number average molecular weight	26000	30000	25000	32000	30000
	Glass transition temperature (°C)	78	61	53	57	78
	Melting point (°C)	-	-	-	-	-
	Acid value (eq/10 <sup>6</sup> g)	27	25	15	38	26

[0071] (Working Examples 1 to 8 and Comparative Examples 1 to 8) The amorphous polyesters A to E shown in Table 3 and the compounding agents a to f shown in Tables 4 and 5 below were mixed in beakers, and each mixture was kneaded on two chilled rolls set to 180°C. Mixing was performed while any resin that had adhered to the chilled rolls was periodically removed with a spatula. After 5 minutes of kneading, the gap between the rolls was set to 0.3 mm (i.e., the sheet thickness was set to 0.3 mm), the molten sheet was taken off from the rolls at a distance of 30 cm, and the sheet takeoff properties were evaluated by visual observation of "sagging" during this procedure. The releasability of the sheet from the roller during this procedure (i.e., the roll release properties) was also evaluated. The evaluation standards are indicated below.

[0072] Sheet releasability:

A: Good releasability from the roll

B: Strong adhesion to rolls/difficulties encountered on release; normal sheet unobtainable.

Sheet takeoff properties:

A: No sagging occurred.

B: Very slight sagging occurred, but within practical application constraints.

C: Sagging of molten sheet under its own weight; a normal sheet unobtainable.

[0073] The transparency of the sheet was evaluated by the following method. Kneading was performed in the same manner as described above using the same two test rolls used in the evaluations of sheet takeoff properties and sheet releasability (roll release properties) described above. After five minutes, the gap between the rolls was set to 0.5 mm and a sheet of 0.5 mm in thickness was obtained. The sheets were cut to a size of 13 cm × 13 cm, and placed between two stacked ferrotype plates (stainless steel hard chrome) in order to increase the smoothness of the sheet surface and keep the sheet thickness constant. The plates were then pressed together at a temperature of 180°C for 90 sec at 12 N/cm<sup>2</sup> and then quenched, resulting in an evaluation sample that was 0.7 mm thick. Determination of haze: The aforementioned evaluation sample was cut to a size of 3 cm × 3 cm to make a test piece. The haze value of the test strip was measured using a model ND-Σ80 manufactured by Nippon Denshi Kogyo Co., Ltd. A lower haze value indicated better transparency. A haze of 15% or less was given a pass ("A"), and samples whose haze exceeded 15% were rejected ("B").

[0074] The results are shown in Tables 4 and 5. In the sheet takeoff properties and transparency evaluation columns, a "—" mark indicates that the evaluation was not performed because the sheet releasability was poor and a normal sheet could not be obtained.

[0075] The antioxidants a to d and the lubricant e in Tables 4 and 5 refer to the following compounds.

a: *tris*(3,5-di-*t*-butyl-4-hydroxybenzyl) isocyanurate

b: Pentaerythritol tetrakis(3-laurylthiopropionate)

c: *Tetrakis*[methylene-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate] methane

d: Distearyl-3,3'-thiodipropionate

e: Tridecylpoly(oxyethylene) phosphate zinc salt (compound (8) in Table 1)

f: Styrene-modified polyethylene wax

The amounts of polyester in Tables 4 and 5 and the amounts of antioxidant and lubricant are given as parts by weight.

[0076]

[Table 4]

		Working Examples								
		1	2	3	4	5	6	7	8	9
Amorphous poly-ester	A	100	100	100					100	
	B				100					
	C					100				
	D							100		
	E						100			100
Anti-oxidant	a	0.2	0.3	0.5	0.5	0.2	0.5	0.3	0.5	0.3
	b	0.1	0.1	0.2	0.1	0.07	0.1	0.07		0.1
	c									0.05
	d									0.1
Lubricant	e	0.5	0.5	1.0	1.0	0.8	0.4	0.8	0.8	0.6
	f	0.1	0.1	0.2	0.2	0.3	0.1	0.2	0.2	0.1
Evaluations	Sheet releasability	A	A	A	A	A	A	A	A	A
	Sheet takeoff properties	A	A	A	B	B	A	B	B	A
	Transparency	A	A	A	A	A	A	A	A	A

[0077]

[Table 5]

		Working Examples							
		1	2	3	4	5	6	7	8
Amorphous poly-ester	A	100	100	100	100				
	B						100		
	C								
	D							100	
	E					100			100
Anti-oxidant	a			0.3			3.0		
	b							0.2	0.2
	c				0.3	0.2			0.5
	d					0.1			0.1
Lubricant	e		0.5		0.5	0.5	0.5	0.8	1.0
	f		0.1		0.1	0.1	0.1	0.2	0.2
Evaluations	Sheet releasability	B	A	B	A	A	A	A	A
	Sheet takeoff properties	-	C	-	C	C	B	C	C
	Transparency	-	A	-	A	B	B	A	B

[0078]

**[Effect of the Invention]** As is evident from the foregoing description, a lubricant is compounded together with a hindered phenolic antioxidant having isocyanurate groups in its molecular skeleton and a thioether antioxidant are compounded with an amorphous polyester in the polyester resin composition of the present invention, which causes the sheet to be releasable from the calendering rolls in calendering. Therefore, the ability of the molten sheet to be transferred from the calendering rolls to the cooling rolls is extremely good, and highly transparent (finished) sheets can be manufactured. In other words, the present invention can provide a hitherto unattainable high-quality polyester resin composition for calendering applications. Worked (finished) sheets are endowed with the good physical properties inherent to polyesters, are highly transparent, and are very safe because they do not contain plasticizers, which are suspected of being endocrine disrupting substances. Moreover, the use of amorphous polyesters enables post-processing to be streamlined to a comparative degree.

(Continued from front page)

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(51) Int. Cl. <sup>7</sup>	Class. Symbols	FI	Subject Codes (Reference)
// B 29 K	67:00	B 29 K	67:00
B 29 L	7:00	B 29 L	7:00
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F Terms (Reference) 4F071 AA46 AA47 AA71 AC05 AC09  
AC10 AC12 AC13 AE05 AE11  
AF03 AF27 AF30 AH03 AH06  
BB04 BC01  
4F204 AA24A AA24C AB06 AB07  
AB19 FA06 FA07 FB02 FF01  
FF06  
4J002 BB032 BB122 CF061 CF081  
CF091 EC068 EF058 EH048  
EH098 EP028 EU196 EV047  
EW048 FD070 FD076 FD077  
FD172 FD178 GA01 GG02  
GJ02